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SYNTHESIS OF ARTICULATED ALL-PARA POLYMERS

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October 1981

Final Report for Period November 1977-December 1979

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MATERIALS LABORATORY
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Articulated all-para polymers with 2,6-benzobisoxazole, 2,6-benzobisthiazole, and 2,6-benzobisimidazole units in the backbone were synthesized by copolycondensation in polyphosphoric acid of 4,6-diamino-1,3-benzenediol dihydrochloride, 2,5-diamino-1,4-benzenedithiol dihydrochloride, and 1,2,4,5-tetraaminobenzene tetrahydrochloride, respectively, with terephthalic acid and reactive diphenoxybenzene monomers. Inherent viscosities of up to 12.57 dL/g (CH_3SO_3H, 25°C, 0.2g/dl) were achieved. The average length of the rod-like all-para segments between the relatively flexible diphenoxybenzene units was

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controlled by the stoichiometry of the copolycondensation reactions. Films which exhibited optical birefringence under crossed polars could be cast from methanesulfonic acid solutions of the polymers. Modulus and tensile strength values as high as 4696 mPa and 93mPa, respectively, were recorded. Thermooxidative stability of the articulated polymers was evaluated by isothermal aging in air at 316°C. Stability for the articulated polybenzobisoxazoles was found to decrease with increased content of the diphenoxybenzene structure. The articulated polybenzobisoxazole structure was shown to be less stable than the analogous polybenzobisthiazole structure but much more stable than the articulated polybenzobisimidazole structure.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Nonmetallic and Composite Materials," Task No. 2303Q3, Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the Materials Laboratory Project Scientist. Co-authors were Dr. R. C. Evers and Dr. F. E. Arnold, Materials Laboratory, (AFWAL/MLBP) and Dr. T. E. Helminiak (AFWAL/MLBC).

This report covers research conducted from November 1977 to December 1979.

The authors wish to thank Mr. G. J. Moore, Mr. J. L. Burkett, and Mr. T. Manek for their contributions to the synthesis operations. The thermal behavior data were contributed by Mr. E. J. Soloski. Mr. C. Benner cast the films and contributed the physical testing data.

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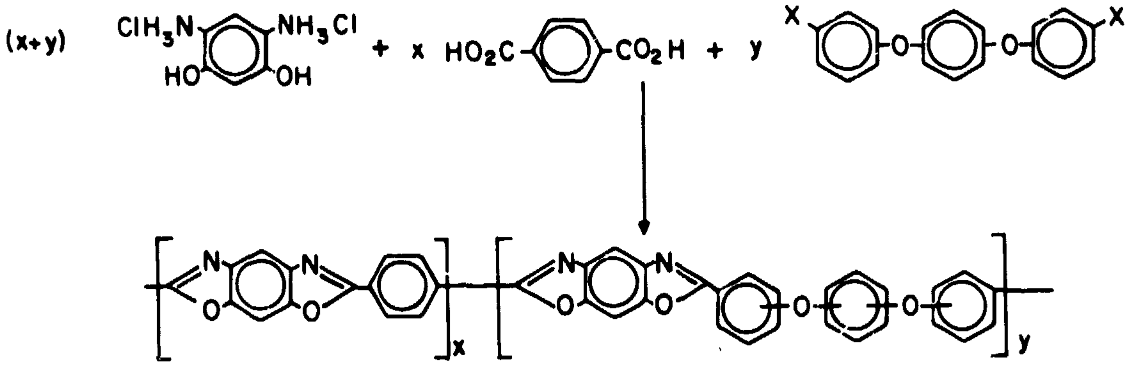
SECTION I
INTRODUCTION

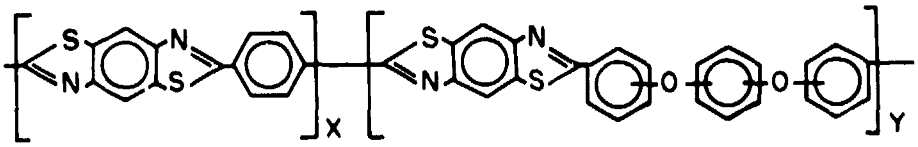
Considerable research effort in recent years has been directed toward the synthesis, characterization, and fabrication of rod-like, thermooxidatively stable polymers for use as high modulus, high strength structural materials in advanced aircraft and aerospace systems. The unique ordering properties of these polymers into liquid crystalline solutions have indicated the potential for fabrication into high modulus bulk forms. Examples of thermooxidatively stable, aromatic-heterocyclic polymers which exhibited liquid crystalline behavior in concentrated solution are poly{[benzo(1,2-d: 5,4-d')bisoxazole-2,6-diyl]-1,4-phenylene} (PBO) (Reference 1), poly{[benzo(1,2-d:4,5-d') bisthiazole-2,6-diyl]-1,4-phenylene} (PBT) (Reference 2), and poly{[benzo (1,2-d:4,5-d')bisimidazole-2,6-diyl]-1,4-phenylene} (PBI) (Reference 3). Two of these all-para, rod-like polymers, PBO and PBT (Reference 4 and 5), have been spun into highly oriented fibers from methanesulfonic acid solutions. Fibers from the latter exhibited exceptionally high modulus and tensile strength values (Reference 5).

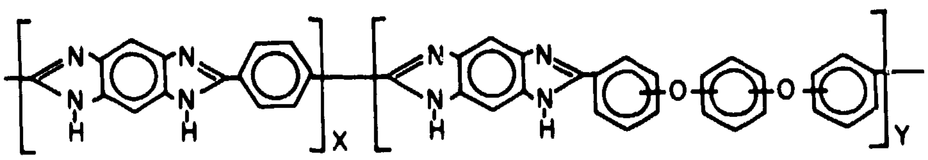
In an attempt to improve the processability of these polymers through improved solubility and to modify the properties of the resultant fabricated specimens, the synthesis of articulated all-para polymers containing 2,6-benzobis-oxazole, -thiazole, and -imidazole units in the polymer backbone was carried out. The synthesis of these articulated-PBOs, -PBTs, and -PBIs was achieved through the introduction into the polymer backbone of a predetermined number of diphenoxybenzene units. The resultant polymers were expected to exhibit differences from the parent polymers (PBO, PBT and PBI) in solubility, thermal characteristics, morphology, etc. Based on the theoretical considerations of Flory (Reference 6) and dependent on the number and isomeric structure of the diphenoxybenzene units (Reference 7), the polymers were also expected to retain the ability to form liquid crystalline solutions.



X= CO_2H, CO_2CH_3, COCl, CN

The initial synthesis effort entailed the preparation of the articulated PBOs through copolycondensation in polyphosphoric acid (PPA) of 4,6-diamino-1,3-benzenediol dihydrochloride with terephthalic acid and appropriately-substituted diphenoxybenzene monomers. The average length of the all-para, rod-like PBO segments was determined by the stoichiometry of the reaction mixture and could be varied by adjusting the mole proportions (x and y, respectively) of terephthalic acid and diphenoxybenzene monomer. Various isomeric diphenoxybenzene structures were used with emphasis initially being placed on incorporation of the -p-C_6H_4-O-p-C_6H_4-O-p-C_6H_4 -(p-p-p) structural isomer into the polymer backbone.





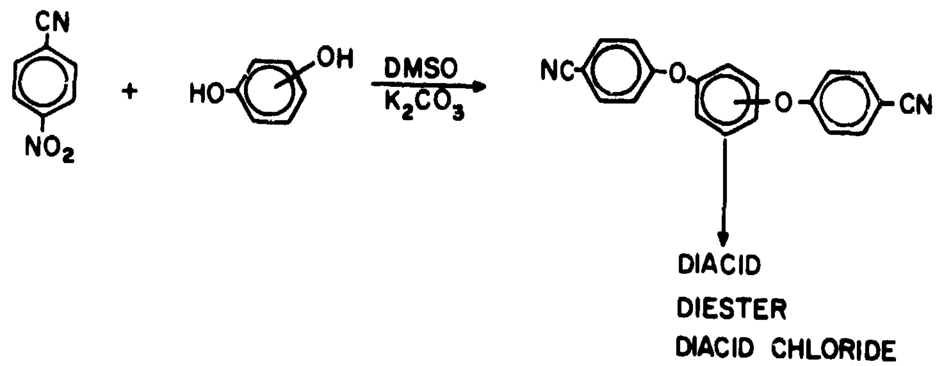
Subsequently, the syntheses of articulated-PBTs and -PBIs were carried out in a similar fashion with 2,5-diamino-1,4-benzenedithiol dihydrochloride and 1,2,4,5-tetraaminobenzene tetrahydrochloride as key monomers. The synthesis and preliminary characterization of the articulated polymers are described below.

SECTION II

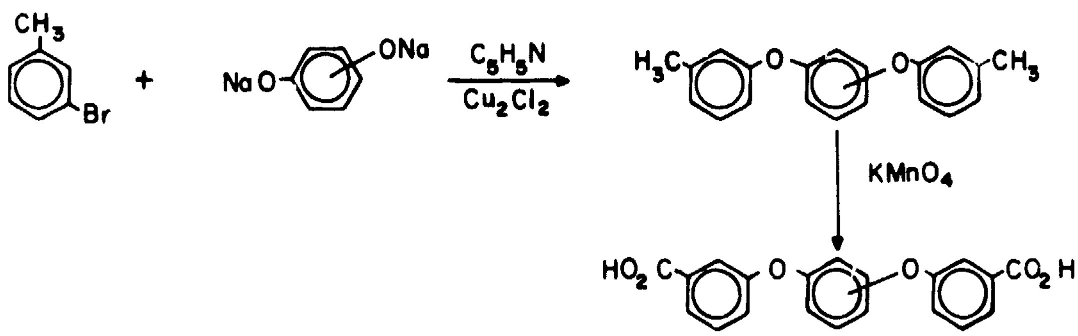
RESULTS AND DISCUSSION

1. MONOMER SYNTHESIS

The key step in the preparation of the p-p-p, p-m-p, and p-o-p isomeric diphenoxybenzene structures entailed the base-promoted reaction of 4-nitrobenzonitrile with hydroquinone, resorcinol, and catechol, respectively. These nitro-displacement reactions were carried out according to the general procedure described by Heath and Wirth (Reference 8). Yields of purified products in the range of 45-85 percent were recorded. These dinitriles [referred to here as p-p-p$(CN)_2$, p-m-p$(CN)_2$, and p-o-p$(CN)_2$] could then be readily converted into the corresponding diacid, dimethyl ester, or diacid chloride derivatives.



However, this synthetic reaction was not applicable to the preparation of the m-p-m and m-m-m diphenoxybenzene structures. The key intermediates in their syntheses were prepared by the cuprous chloride-catalyzed reaction of sodium m-cresylate with p-dibromobenzene and m-dibromobenzene, respectively. Alternatively, these compounds could be prepared in lower yield by the reaction of m-bromotoluene with the disodium salts of hydroquinone and resorcinol (Reference 9). The resultant dimethyl compounds then underwent oxidation with potassium permanganate to give the corresponding diacids [m-p-m($CO_2H)_2$ and m-m-m(CO_2H_2] which could be converted to the dinitrile or diacid chloride derivatives.



2. POLYMER SYNTHESIS

In order to determine the solubility and demonstrate the reactivity of the diphenoxybenzene monomers, initial polymer synthesis efforts were directed toward the polycondensation of 4,6-diamino-1,3-benzenediol dihydrochloride with p-p-p(CO_2H_2) and its derivatives. The results are shown in Table 1. The polycondensation reactions were run in freshly prepared PPA at a solids content of approximately one percent by weight. After dehydrochorination of the dihydrochloride salt was effected at 80-110°C over a period of several hours, the reaction temperature was gradually raised over several days to 190°C. Both the diacid monomer

(Trial No. 1) and the dimethyl ester monomer (Trial No. 3) exhibited limited solubility in PPA. Suspended, undissolved monomer was still present at the termination of the polycondensation reaction. This factor probably limited the polymer DP and led to polymer discoloration due to monomer decomposition at higher temperatures. In a sulfolane/PPA reaction medium (Trial No. 2), rapid and complete dissolution of the diacid monomer took place but did not lead to an improvement in the η_{inh} or quality of the polymer. However, polycondensation reactions in PPA involving the dinitrile- or diacid chloride-derivatives (Trial Nos. 4 and 5, respectively) quickly became homogeneous and yielded golden-colored polymer albeit of no greater η_{inh}. Polycondensation of p-m-p$(CO_2H)_2$ and p-m-p$(CN)_2$ with 4,6-diamino-1,3-benzenediol dihydrochloride (Trial Nos. 6 and 7, respectively) resulted in the formation of extremely viscous, apparently homogeneous solutions of polymer in PPA. Upon work-up, the isolated polymers proved to be insoluble in a variety of solvents. The reason for this insolubility has not been determined.

Synthesis of the articulated PBOs was carried out by copolycondensation in PPA of 4,6-diamino-1,3-benzenediol dihydrochloride with terephthalic acid and the diphenoxybenzene monomers. The results are shown in Table 2. After dehydrohalogenation was complete, polycondensation of terephthalic acid and 4,6-diamino-1,3-benzenediol was allowed to proceed at 130° to give a clear yellow solution. Addition of the diphenoxybenzene monomer followed by a gradual increase in the reaction temperature over several days to 190-210°C yielded soluble fibrous polymers which varied in color from pale yellow to brown. The latter color was observed when a large mole proportion of relatively insoluble p-p-p$(CO_2H)_2$ was used (Trial No. 3). In the interest of polymer quality, the more soluble and consequently more reactive diacid chloride- and dinitrile-derivatives were usually used. The articulated PBOs generally exhibited higher η_{inh} than the homopolymers described in Table 1. This increase was most pronounced in the articulated PBOs containing small mole proportions (0.03 to 0.10) of the diphenoxybenzene structure; a maximum η_{inh} of 9.88 dL/g was recorded. Substantial

TABLE 1

POLYCONDENSATION OF 4,6-DIAMINO-1,3-BENZENEDIOL DIHYDROCHLORIDE AND DIPHENOXYBENZENE MONOMER

Trial No.	Diphenoxybenzene Monomer	η_{inh}-dL/g[b]
1.	p-p-p$(CO_2H)_2$	1.90
2.[a]	p-p-p$(CO_2H)_2$	1.60
3.	p-p-p$(CO_2CH_3)_2$	0.67
4.	p-p-p$(CN)_2$	1.93
5.	p-p-p$(COCl)_2$	1.97
6.	p-m-p$(CO_2H)_2$	insol.[c]
7.	p-m-p$(CN)_2$	insol.[c]

(a) 1.5 PPA/sulfolane (w/w) used as polycondensation solvent.

(b) CH_3SO_3H, $25^\circ C$, 0.2 g/dL

(c) Solvents tested include CH_3SO_3H, H_2SO_4, $ClSO_3H$, m-cresol

TABLE 2

COPOLYCONDENSATION OF 4,6-DIAMINO-1,3-BENZENEDIOL DIHYDROCHLORIDE WITH TEREPHTHALIC ACID AND DIPHENOXYBENZENE MONOMER

Trial No.	Diphenoxybenzene Monomer	y - Mole Proportion	η_{inh} - dL/g (b)
1.	p-p-p$(CN)_2$	0.50	1.41
2.	p-p-p$(CN)_2$	0.25	1.99
3.	p-p-p$(CO_2H)_2$	0.25	1.94
4.	p-p-p$(COCl)_2$	0.25	2.34
5.	p-p-p$(CN)_2$	0.10	3.18
6.(a)	p-p-p$(CN)_2$	0.10	7.08
7.(a)	p-p-p$(CN)_2$	0.05	8.58
8.	p-p-p$(CN)_2$	0.03	6.75(c)
9.	p-m-p$(CN)_2$	0.50	insol.
10.	p-m-p$(CN)_2$	0.25	insol.
11.	p-m-p$(COCl)_2$	0.10	4.37
12.	p-m-p$(CN)_2$	0.05	3.77
13.	p-m-p$(CN)_2$	0.03	9.88
14.	p-o-p$(CN)_2$	0.10	5.44
15.	p-o-p$(CN)_2$	0.05	6.74
16.	p-o-p$(CO_2H)_2$	0.05	7.73
17.	p-o-p$(CN)_2$	0.03	6.86
18.	m-p-m$(CN)_2$	0.05	7.67
19.	m-m-m$(COCl)_2$	0.03	7.84

(a) Concentration = 2.4-2.6%(w/w)

(b) CH_3SO_3H, 25°C, 0.2 g/dL

(c) $[\eta]$ = 8.10 dL/g(CH_3SO_3H, 25°C)

differences in the solution viscosity-polymer DP relationships as well as increased polymer DP were probably responsible for the increase in η_{inh} values. In general, the solution viscosity values reported for the articulated PBOs were substantially higher than those reported for PBO synthesized by a similar experimental procedure (programmed heating rate), (References 1 and 10), and equivalent to those obtained from PBO prepared by isothermal polycondensation reactions (Reference 11).

As in the case of the polycondensation reactions of p-m-p$(CN)_2$ and p-m-p$(CO_2H)_2$ with 4,6-diamino-1,3-benzenediol described above, the copolycondensation reactions of p-m-p$(CN)_2$ and p-m-p$(COCl)_2$ gave rise to extremely viscous, apparently homogeneous reaction mixtures (Trial Nos. 8-12). The isolated articulated PBOs, however, were soluble only when mole proportions of 0.10 or less of the diphenoxybenzene monomers were used.

Although the copolycondensation reactions were generally run at a solids content of approximately one percent, higher concentrations could be used (Trial Nos. 6 and 7); high η_{inh} were obtained even though stirring could not be effectively employed in the latter stages of the reaction.

Synthesis of the articulated PBTs was performed under conditions similar to those described for preparation of the articulated PBOs. Loss of hydrogen chloride occurred at 60-80°C and a clear yellow solution formed upon several hours of heating at 130°C. Addition of a readily soluble diphenoxybenzene monomer [p-o-p$(CN)_2$, m-p-m(CN_2)] followed by a rapid temperature increase to 150°C and a gradual increase to 195-200°C over several days yielded yellow-orange, fibrous polymers. The results are summarized in Table 3.

Several articulated PBIs were also synthesized in a similar manner to yield red-brown, fibrous polymers in high yields. The results are summarized in Table 4. Although small amounts (approximately 10%) of

TABLE 3

COPOLYCONDENSATION OF 2,5-DIAMINO-1,4-BENZENEDITHIOL DIHYDROCHLORIDE WITH TEREPHTHALIC ACID AND DIPHENOXYBENZENE MONOMER

Trial No.	Diphenoxybenzene Monomer	y-Mole Proportion	η_{inh}- dL/g (a)
1.	p-o-p$(CN)_2$	0.10	7.97
2.	m-p-m$(CN)_2$	0.10	12.02
3.	m-p-m$(CN)_2$	0.03	12.57

(a) CH_3SO_3H, 25°C, 0.2 g/dL

TABLE 4

COPOLYCONDENSATION OF 1,2,4,5-TETRAAMINOBENZENE TETRAHYDROCHLORIDE WITH TEREPHTHALIC ACID AND DIPHENOXYBENZENE MONOMER

Trial No.	Diphenoxybenzene Monomer	y-Mole Proportion	η_{inh}- dL/g (a)
1.	p-p-p$(COCl)_2$	0.10	9.92
2.	p-o-p$(CN)_2$	0.10	9.13

(a) CH_3SO_3H, 25°C, 0.2 g/dL

insolubles were present, the articulated PBIs exhibited solubility in methanesulfonic acid. By comparison, PBI prepared by the polycondensation of 1,2,4,5-tetraaminobenzene tetrahydrochloride with terephthalic acid in PPA is reported to be completely insoluble (Reference 3).

3. POLYMER CHARACTERIZATION

The articulated -PBOs, -PBTs, and -PBIs described above were soluble in methanesulfonic-, chlorosulfonic-, and sulfuric-acid. They were insoluble in all aprotic solvents tested. Solution phase equilibria studies of the articulated PBOs in methanesulfonic acid are currently underway in another laboratory to determine their capability to order into liquid crystalline solutions and to determine their solubility relative to PBO. Preliminary results indicate that markedly enhanced solubility is not achieved by the introduction of diphenoxybenzene structures into the PBO backbone. Nematogenic solutions in methanesulfonic acid at 25°C can be obtained if the mole proportion of diphenoxybenzene structure is 0.05 or less (Reference 12).

Solution viscosity data on the articulated polymers were determined using methanesulfonic acid as a solvent. The η_{inh} or [η] values recorded were found to be quite dependent upon the work-up history of the respective polymer samples and were found to decrease substantially upon dissolution and reprecipitation of the polymer. For example, an articulated PBO (Trial No. 14) initially exhibited an η_{inh} of 5.44 dL/g. Dissolution and reprecipitation from methanesulfonic acid into methanol resulted in an η_{inh} of 3.57 dL/g. Although the possibility of polymer chain scission existed, irreversible molecular aggregation of the polymer chains during the dissolution-reprecipitation process was a more likely cause for this phenomenon. Similar changes in solution viscosity data have been observed with PBO and PBT (References 11 and 12).

As would be expected, the presence of the diphenoxybenzene structure in the articulated polymers resulted in decreased thermooxidative stability compared to the parent polymers. This decrease in thermooxidative stability could be readily determined by isothermal aging studies in air at elevated temperatures. Articulated PBOs, for example, in air at 316°C (Figure 1) exhibited greater weight losses as the diphenoxybenzene unit content increased.

Isothermal aging in air at 316°C (Figure 2) of articulated-PBOs, -PBTs, and -PBIs of analogous structure demonstrated the superior thermooxidative stability of the articulated PBTs and the relatively poor thermooxidative stability of the articulated PBIs compared to the articulated PBOs. This order of thermooxidative stability (PBT>PBO>>PBI) was also observed in the parent polymers (Reference 13).

Films which exhibited optical birefringence under crossed polars could be cast from methanesulfonic acid solutions of the articulated polymers. Tensile strength and modulus values for films of articulated PBOs are shown in Table 5. In comparison, continuous films could not be case from methanesulfonic acid solutions of the parent polymers. Excessive shrinking led to extensive cracking of these films.

4. CONCLUSIONS

Articulated-PBOs, -PBTs, and -PBIs can be synthesized in moderate-to-high molecular weight through incorporation of diphenoxybenzene units into the polymer backbone. This is best achieved in the copolycondensation reactions through the use of the dinitrile or diacid chloride of the appropriate diphenoxybenzene structure. Incorporation of the flexible diphencxybenzene unit into the polymers does not lead to observable solubility in aprotic solvents. As expected, thermooxidative stability of the articulated polymers decreases with increased content of the diphenoxybenzene structure. The thermooxidative stability of the articulated PBIs is quite poor compared to the articulated PBOs and PBTs.

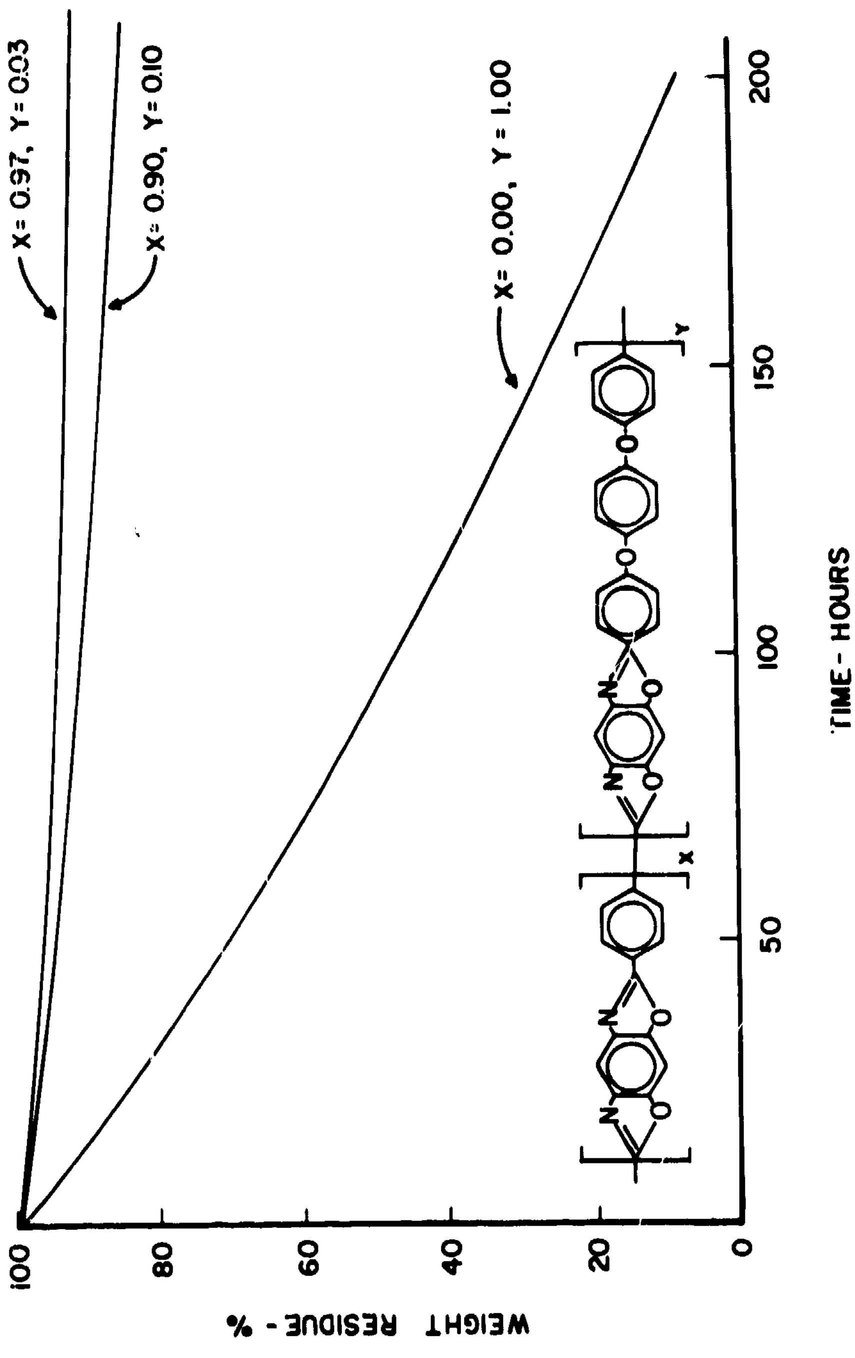


Figure 1. Isothermal Aging in Air at 316°C for Articulated PBOs.

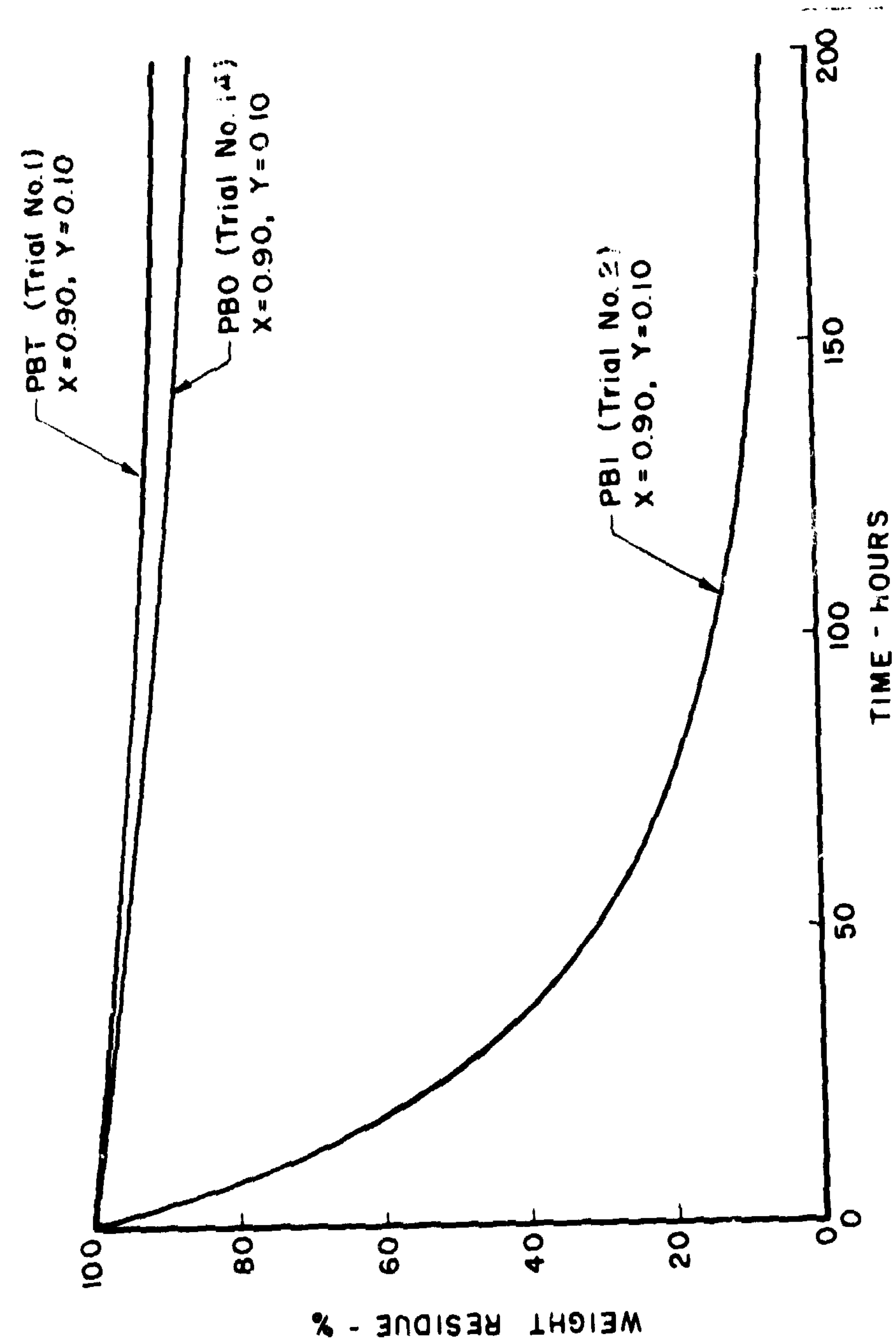


Figure 2. Isothermal Aging in Air at 316°C for Articulated -PBO, -PBT, and -PBI.

TABLE 5

FILM PROPERTIES OF ARTICULATED PBOS

Trial No.	Diphenoxybenzene Structure	y-Mole Proportion	Tensile Strength-mPa	Modulus-mPa
6.	p-p-p	0.10	56	1558
14.	p-o-p	0.10	77	3765
15.	p-o-p	0.05	49	2317
17.	p-o-p	0.03	62	2365
18.	m-p-m	0.05	93	3068
19.	m-m-m	0.03	52	4696

Continuous films of the articulated polymers can be cast from methanesulfonic acid. In comparison, films cast from solutions of the parent polymers show extensive cracking because of excessive shrinkage.

Continuing studies are underway to further assess the potential of the articulated PBOs and PBTs for fabrication into high modulus specimens for use in severe environments. In an inhouse synthesis effort, more thermooxidatively stable articulated PBOs and PBTs are being synthesized through the introduction of aromatic or heterocyclic flexible units into the PBO or PBT backbone. In a related contractural effort, solution phase equilibria studies are addressing the capability of the articulated PBOs and PBTs to order into liquid crystalline solutions. The film forming capability of the articulated PBTs relative to PBT is also being investigated through a film extrusion process.

SECTION III

EXPERIMENTAL

1. MONOMER SYNTHESIS

The requisite monomers were either obtained from commercial sources and purified as necessary or synthesized according to the procedures described below:

Terephthalic acid was obtained from Amoco Chemicals Corporation. The monomer grade terephthalic acid was finely ground to an average particle size of 95% < 10μm (courtesy of Dr. J. F. Wolfe) (Reference 2).

1,2,4,5-Tetraaminobenzene tetrahydrochloride was obtained from Burdick and Jackson. It was carefully recrystallized from hydrochloric acid and dried prior to use.

4,6-Diamino-1,3-benzenediol dihydrochloride was prepared by Midwest Research Institute according to the procedure of Wolfe and Arnold (Reference 14). It was also purified by recrystallization from hydrochloric acid.

2,5-Diamino-1,4-benzendithiol dihydrochloride was prepared by Dr. J. F. Wolfe according to his published procedure (Reference 2).

4,4'-(p-Phenylenedioxy)dibenzoic acid [p-p-p($CO_2H)_2$]. 4,4-(p-Phenylenedioxy) dibenzonitrile (Reference 15) (15.0 g, 0.048 mol) and potassium hydroxide pellets (45.0 g, 0.800 mol) were stirred under nitrogen in 375 mL of redistilled ethylene glycol. The wl ite slurry was heated to reflux to produce a vigorous evolution of · wonia. The resultant pale yellow solution became cloudy after a few .ainutes and a flocculent white precipitate was formed. After 20 hours at 175°C, 75 mL of ethylene glycol was distilled off and the reaction mixture was cooled in an ice bath. The white precipitate was isolated by filtration and washed on the frit with isopropanol. The crude dipotassium salt (18.3 g)

thus isolated was dissolved in 200 mL of dilute potassium hydroxide solution. After being refluxed for thirty minutes, the cloudy solution was treated with charcoal, filtered, and reduced in volume to 90 mL. Cooling of the solution gave 15.6 g of the dipotassium salt which was isolated by filtration and washed on the frit with isopropanol. Dissolution of this salt in 200 mL of water gave a hazy solution which was heated to reflux and then acidified with concentrated hydrochloric acid. The resultant white slurry was refluxed for four hours, cooled, and filtered to give 13.5 g of the crude diacid. After extraction of the crude diacid with a liter of refluxing tetrahydrofuran, 1.2 g of insoluble material remained. The tetrahydrofuran solution was diluted with an equal volume of hexane to precipitate the diacid (10.4 g). Recrystallization from 900 mL of dioxane (charcoal) gave 7.2 g (43% yield) of powdery white product, mp 331-333°C (Reference 16; mp 313-315°C). The product could not be further purified by recrystallization. Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03;MW, 350. Found: C, 68.24; H, 4.11; MW, 350 (mass spectrum).

<u>4,4'-(p-Phenylenedioxy)dibenzoyl chloride [p-p-p($COCl)_2$] and 4,4'-(p-phenylenedioxy)dimethyl benzoate) [p-p-p($CO_2CH_3)_2$]</u> were prepared from the diacid as described by Malichenko and coworkers (Reference 16).

<u>4,4'-(m-Phenylenedioxy)dibenzonitrile [p-m-p$(CN)_2$]</u>. Resorcinol (11.0 g, 0.100 mol) and dry potassium carbonate (82.8 g, 0.600 mol) were stirred for two hours at room temperature under nitrogen in 300 mL of freshly distilled dimethyl sulfoxide. 4-Nitrobenzonitrile (32.56 g, 0.220 mol) was then added and the reaction temperature was raised to 75°C for 20 hours. The dark solution was poured with vigorous stirring into 1500 mL of ice water and the resultant suspension was stirred for an additional hour. The grey, lumpy product was isolated by filtration, washed well with water, and allowed to dry overnight on the frit. It was taken up in 1600 mL of isopropanol (some insoluble material) and the solution was treated with

charcoal. Reduction of the solution volume to 700 mL followed by cooling in ice water gave 25.5 g (82% yield) of white crystalline product, mp 123.5-125°C (Reference 17; mp 123-124°C).

<u>4,4'-(m-Phenylenedioxy)dibenzoic acid [p-m-p(CO_2H)$_2$]</u> was prepared by hydrolysis of the dinitrile in a procedure very similar to that described above for the p-p-p isomer. Recrystallization from dioxane gave a 64% yield of powdery white product, mp 300-302°C.

Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03; MW, 350. Found: C, 68.36; H, 3.80; MW, 350 (mass spectrum).

<u>4,4'-(m-Phenylenedioxy)dibenzoyl chloride [p-m-p(COCl)$_2$]</u> was prepared through reaction of the corresponding diacid (7.0 g, 0.020 mol) with phosphorous pentachloride (10.5 g, 0.074 mol) in 37 g of phosphorous oxychloride. After the solution was allowed to reflux for two hours, the phosphorous oxychloride was distilled off under reduced pressure and the residue was extracted with 75 mL of hexane. Recrystallization from hexane gave 2.40 g (31% yield) of product, mp 77-78.5°C.

Anal. Calcd for $C_{20}H_{12}Cl_2O_4$: C, 62.04; H, 3.13; Cl, 18.31; MW, 387. Found: C, 62.40; H, 3.16; Cl, 17.98; MW, 387 (mass spectrum).

<u>4,4'-(o-Phenylenedioxy)dibenzonitrile [p-o-p(CN)$_2$]</u> was prepared by reaction of the dipotassium salt of catechol with 4-nitrobenzonitrile in dimethyl sulfoxide. Reaction conditions and work-up were similar to that described for the analogous p-m-p isomer. Successive recrystallizations from heptane and isopropanol afforded a 45% yield of white crystals, mp 116.5-117.5°C.

Anal. Calcd for $C_{20}H_{12}N_2O_2$: C, 76.91; H, 3.87; N, 8.97; MW, 312. Found: C, 76.97; H, 3.65; N, 8.75; MW, 312 (mass spectrum).

<u>3,3'-(p-Phenylenedioxy)dibenzonitrile [m-p-m(CN)$_2$]</u>. To a solution of 3,3'-(p-phenylenedioxy)ditoluene (Reference 18) (9.9 g, 0.034 mol) in 255 mL of pyridine was added a slurry of potassium permanganate (42.6 g, 0.270 mol) in 150 mL of water. After being stirred for an hour at room temperature, the reaction mixture was heated at 70°C overnight. The cooled reaction mixture was diluted with 125 mL of water and then made strongly acidic by the addition of 280 mL of concentrated hydrochloric acid. The acidified reaction mixture was heated to 70°C for an hour, cooled, and then filtered. The filter cake was thoroughly washed with water and allowed to dry on the frit. This solid was placed in a continuous extraction apparatus and extracted with ether and then with methylene chloride. Evaporation of the combined extracts gave 9.4 g of crude material. Two recrystallizations from glacial acetic acid yielded 6.7 g (56% yield) of white powdery 3,3'-(p-phenylenedioxy)dibenzoic acid, mp 305-313°C (Reference 19; 300-308°C).

Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03; MW, 350. Found: C, 68.79; H, 3.96; MW, 350 (mass spectrum).

The diacid (24.0 g, 0.069 mol) was refluxed under nitrogen with 80 ml of thionyl chloride for five hours to give a clear tan solution. Excess thionyl chloride was stripped off under reduced pressure and the residue was distilled to give 18.3 g of pale yellow liquid, bp 220-234°C/ 2.5 mm Hg. The solidified crude product was recrystallized from heptane (charcoal) to give 12.2 g (46% yield) of 3,3'-(p-phenylenedioxy)dibenzoyl chloride as white needles, mp 73.5-76°C.

Anal. Calcd for $C_{20}H_{12}Cl_2O_4$: C, 62.04; H, 3.13; Cl, 18.31; MW, 387. Found: C, 62.03; H, 2.87; Cl, 18.24; MW, 387 (mass spectrum).

The diacid chloride (20.0 g, 0.052 mol) was dissolved in 200 ml of ether and the resultant solution was added dropwise to 150 ml of vigorously stirred concentrated ammonium hydroxide at 0-5°C. When addition was complete after two hours, the white slurry was allowed to warm to room temperature. After two hours at room temperature, the reaction mixture was

filtered and the white filter cake was washed with ammonium hydroxide and with water. The filter cake was allowed to dry on the frit overnight and was then recrystallized from isopropanol to give 9.7 g (54% yield) of 3,3'-(p-phenylenedioxy) dibenzamide, mp 244-246°C.

Anal. Calcd for $C_{20}H_{16}N_2O_4$; C, 68.96; H, 4.62; N, 8.04; MW, 348. Found: C, 68.86; H, 4.36; N, 8.15; MW, 348 (mass spectrum).

The diamide (9.7 g, 0.028 mol) was dissolved in 160 mL of N, N-dimethylformamide. Thionyl chloride (25 ml) was added dropwise to the solution over a period of three hours with the temperature being maintained at 0-5°C. During the addition period, the reaction mixture changed from a clear, water-white solution to a milky suspension and then to a clear yellow solution. The solution was stirred at ice bath temperature for six hours and then was poured over ice. Acidification of the aqueous solution was effected with concentrated hydrochloric acid. The addition of 200 mL of water followed by filtration gave a white filter cake which was washed repeatedly with water. After being allowed to dry on the frit, the crude white product (7.9 g, mp 116-124°C) was recrystallized once from heptane and three times from isopropanol to give 3,3'-(p-phenylenedioxy)dibenzonitrile as fine white needles, mp 139.5-141°C.

Anal. Calcd for $C_{20}H_{12}N_2O_2$; C, 76.91; H, 3.87; N, 8.97; MW, 312. Found: C, 76.81; H, 3.58; N, 8.74; MW, 312 (mass spectrum).

<u>3,3'-(m-Phenylenedioxy)dibenzoyl chloride [m-m-m(COCl)$_2$].</u> m-Cresol (27.5 g, 0.254 mol) and sodium methoxide (13.0 g, 0.242 mol) were refluxed with stirring under nitrogen in 350 mL of benzene for ninety minutes. The benzene was then stripped off under reduced pressure and 500 mL of dry pyridine was added to the white sodium salt. m-Dibromobenzene (27.9 g, 0.119 mol) and cuprous chloride (9.0 g) were added to the reaction mixture which was then refluxed for 5 days. Approximately 400 mL of pyridine was then distilled from the reaction flask and the residue was poured into ice water. Following acidification of the aqueous slurry with concentrated hydrochloric acid, the insolubles were isolated by

filtration. Both the filter cake and the filtrate were extracted repeatedly with light petroleum ether and the combined extracts were washed once with water. The petroleum ether extracts were dried over anhydrous magnesium sulfate and the solvent was stripped off under reduced pressure. Distillation of the dark brown residual oil (38.4 g) afforded 23.5 g (68% yield) of pure 3,3'-(m-phenylenedioxy)ditoluene, bp 159-163° C/3 mm Hg.

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.74; H, 6.23; MW, 290. Found: C, 82.54; H, 6.02; MW, 290 (mass spectrum).

Subsequent oxidation of this intermediate with potassium permanganate in an aqueous pyridine reaction medium afforded a low yield of white 3,3'-(m-phenylenedioxy)dibenzoic acid which exhibited a mp of 269-274°C after repeated recrystallization from glacial acetic acid.

Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03; MW, 350. Found: C, 68.69; H, 3.76; MW, 350 (mass spectrum).

The diacid was subsequently refluxed under nitrogen with thionyl chloride. Reaction conditions and work-up procedures very similar to those described above for the analogous m-p-m isomer gave a 61% yield of 3,3'-(m-phenylenedioxy) dibenzoyl chloride as white crystals, mp 117.5-120°C.

Anal. Calcd for $C_{20}H_{12}Cl_2O_4$: C, 62.04; H, 3.13; Cl, 18.31; MW, 387. Found C, 62.22; H, 2.97; Cl, 18.44; MW, 387 (mass spectrum).

2. POLYMER SYNTHESIS

Typical experimental procedures for the synthesis of the articulated-PBOs, -PBTs, and -PBIs are given below:

Articulated PBO (Trial No. 7) A slurry of terephthalic acid (0.790 g, 4.75 mmol) and 4,6-diamino-1,3-benzenediol dihydrochloride (1.065 g, 5.00 mmol) in 75 g of freshly prepared PPA was stirred under nitrogen at

90-110°C for four hours to effect dehydrochlorination. The temperature was raised to and held at 130°C for 20 hours. 4,4'-(p-Phenylenedioxy) dibenzonitrile (0.079 g, 0.25 mmol) and 80 g of PPA were added to the clear yellow solution and the resultant slurry was heated at 150°C for 19 hours. The clear red reaction mixture was then heated at 175°C for 7 hours, 185°C for 2 hours, and 195°C for 16 hours. Addition of the cooled, extremely viscous solution to water gave fibrous polymer which was vigorously washed three times with water in a blender and extracted for three days with water in a continuous extraction apparatus. Drying at room temperature/0.01 mm Hg for 20 hours and at 145°C/0.01 mm Hg for six hours yielded 1.1g (92% yield) of pale yellow polymer; η_{inh} = 8.58 dL/g (methanesulfonic acid, 25°C, 0.2 g/dL).

Anal. Calcd for $(C_{14}H_6N_2O_2)_{0.95}(C_{26}H_{14}N_2O_4)_{0.05}$: C, 72.06; H, 2.63; N, 11.50. Found: C, 72.99; H, 2.19; N, 11.68.

Articulated PBT (Trial No. 3). Terephthalic acid (0.806 g, 4.85 mmol) and 2,5-diamino-1,4-benzenedithiol dihydrochloride (1.226 g, 5.00 mmol) were stirred with 110 g of freshly prepared PPA at room temperature under nitrogen for two hours. The viscous white slurry was then heated at 70°C for six hours to effect dehydrochlorination and the temperature was then gradually raised over two hours to 130°C. 3,3'-(p-Phenylenedioxy) dibenzonitrile (0.047 g, 0.15 mmol) and additional 104 g of PPA were added and stirring was continued at 130°C for three hours to give a clear, deep red solution. The solution was then heated with stirring as follows: 150°C for 16 hours; 185°C for 8 hours and 200° for 16 hours. After several hours at 200°C, the viscous reaction mixture was climbing the stirrer shaft and stirring was not effective. The cooled polymerization mixture was added to a liter of water in a blender. The precipitated polymer was vigorously washed three times with water in the blender and was extracted with water in a continuous extraction apparatus for three days. Drying at room temperature/0.01 mm Hg for 16 hours and 188°C/0.01 mm Hg for 6 hours yielded 1.2 g (91% yield) of fibrous yellow-orange polymer; η_{inh} = 12.57 dL/g (methanesulfonic acid, 25°C, 0.2 g/dL).

Anal. Calcd for $(C_{14}H_6N_2S_2)_{0.97}(C_{26}H_{14}N_2O_2S_2)_{0.03}$: C, 63.44; H, 2.31; N, 10.30; S, 23.59. Found: C, 63.90; H, 1.86; N, 10.44; S, 23.67.

Articulated PBI (Trial No. 1). 1,2,4,5-Tetraaminobenzene tetrahydrochloride (1.420 g, 5.00 mmol) and terephthalic acid (0.748 g, 4.50 mmol) were stirred in 105 g of freshly prepared PPA at 90-100°C for two hours. When evolution of HCl subsided, the temperature was slowly raised to 130°C to give a clear yellow solution. 4,4'-(p-Phenylenedioxy) dibenzoyl chloride (0.194 g, 0.50 mmol) was added along with an additional 65 g of PPA. The reaction mixture was heated as follows: 150°C for four hours (clear red solution); 175°C for 16 hours; 190°C for 8 hours and 210°C for 4 hours. The polymer solution exhibited a blue coloration and was climbing the stirrer shaft well before the end of the heating period. The cooled reaction mixture was added to water and the precipitated polymer was vigorously washed with water three times in a blender. Extraction with water in a continuous extraction apparatus for three days followed by drying at room temperature/0.01 mm Hg for 16 hours and 100°C/0.01 mm Hq for four hours yielded 1.1 g (87% yield) of red-brown polymer; η_{inh} = 9.92 dL/g (methanesulfonic acid, 25°C, 0.2 g/dL). This sample contained approximately ten percent by weight of insoluble polymer.

Anal. Calcd for $(C_{14}H_8N_4)_{0.90}(C_{26}H_{16}N_4O_2)_{0.10}$: C, 72.84; H, 3.53; N, 22.35. Found: C, 70.81; H, 3.31; N, 20.60.

3. FILM PREPARATION AND CHARACTERIZATION

Films could be prepared from the articulated polymers by vacuum casting from dilute solutions. The general procedure followed was to prepare a two percent polymer solution in methanesulfonic acid and put the solution in a specially fabricated circular flat-bottomed casting dish. The dish was then placed and leveled in the bottom of a sublimator. The cold finger of the sublimator was maintained at 25°C and sublimator was continuously evacuated and heated to 60°C to facilitate the removal of the

methanesulfonic acid. After the films were formed and removed from the casting dish, they were generally dried at 100°C in a vacuum oven for 24 to 48 hours. The films produced were approximately 5-cm in diameter and 5.0×10^{-3} cm in thickness. Most of the films retained approximately 15 percent residual solvent. Mechanical property data for an average of five test specimens was obtained on an Instron Tensile Tester, Model 1102, at 0.02 in./min.

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